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STUDY OF THE FORMATION REACTION OF POLYBENZIMIDAZOLES

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The mechanism of the synthesis of polybenzimidazoles is investigated on the example of the polycondensation reaction of 3,3'-diaminobenzidine with the diphenyl ester of sebacic acid. Thermographic analyses showed the reaction temperature to be of major significance. An increase led to a sharp rise in molecular weight of the polymer and shortening of the reaction time. During the first stages, the reaction is of the equilibrium kind, accompanied by cessation of chain growth; during later stages, the equilibrium character is lost due to the presence of extremely stable benzimidazole rings in the macromolecules. AUTHOR

A new class of polymers - polybenzimidazoles - was recently synthesized by Brinker and Robinson (Bibl.1) by reacting bis-ortho-diaminophenyls with aliphatic dicarboxylic acids, and by Vogel and Marvel (Bibl.2) with aromatic acids. It turned out that these polymers are distinguished by their high chemical and thermal resistance, particularly the latter with their completely aromatic structure.

The aim of the present investigation was to clarify certain patterns and mechanisms of this process. The polycondensation reaction of 3,3'-diaminobenzidine with the diphenyl ester of sebacic acid was selected for this purpose. Polycondensation was accomplished by heating the reagents in a nitrogen stream

* Numbers in the margin indicate pagination in the original foreign text.

and, in some cases, additionally in vacuum.

The obtained quantitative yields of polymers comprised yellow-brown vitreous products which were soluble at room temperature only in conc. sulfuric and

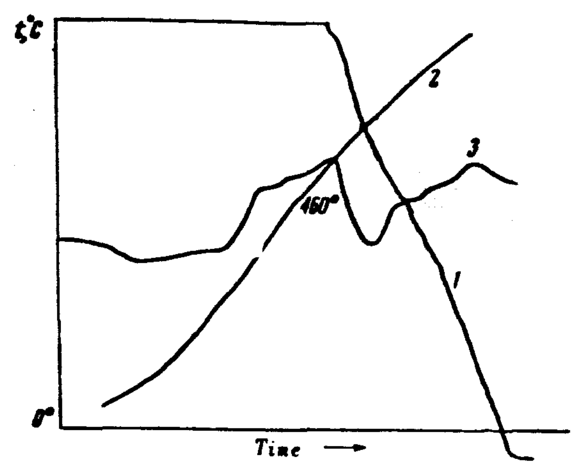


Fig.1 Thermographic Analysis of Polybenzimidazole Synthesized at 270° C, Reaction Time 3 Hours
1 - Weight change of polymer on heating; 2 - Temperature rise with time; 3 - Thermogram. At 630° C the weight loss of the polymer is 92.5%.

formic acids. On heating, they become partially soluble in dimethylformamide and glacial acetic acid; they are not soluble in hydrochloric acid, cresol, and benzyl alcohol. The viscosity of all the synthesized polymers was determined on 0.5% solutions in conc. formic acid. In addition, their elementary composition was determined and their infrared (IR) and ultraviolet (UV) spectra were measured. Further, roentgenograms were taken and thermomechanical curves plotted.

Figure 1 presents the results of a thermographic investigation of poly-2,2' (octamethylene)-5,5'-dibenzimidazole, obtained by heating for 4 hrs at 270° C. The heating rate was 17° C/min. Curve 1, showing the weight loss of the polymer at high temperatures (21 mg), indicates that this polymer decomposes only at 450 - 470° C.

As revealed by the findings, the reaction temperature is of major significance for the process of polycondensation of 3,3'-diaminobenzidine with diphenylsebacate. The increase in reaction temperature leads to a sharp increase in

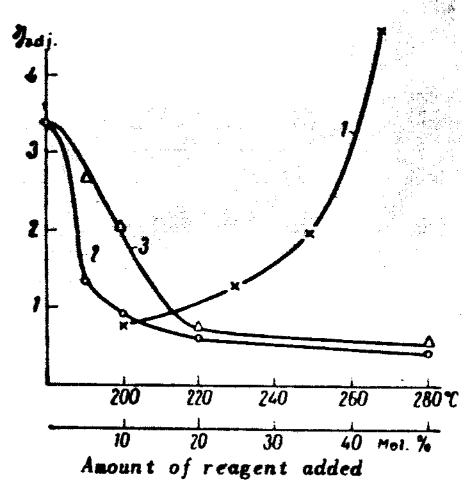
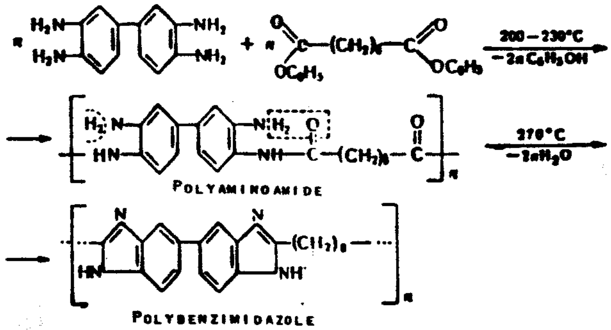


Fig.2 Adjusted Viscosity of Solution of Poly-2,2'-(Octamethylene)-5,5'-Dibenzimidazole in Formic Acid as a Function of:
1 - Polycondensation temperature (heating time 3 hrs); 2 - Amount of stearic acid added; 3 - Amount of α-naphthylamine added.

molecular weight (viscosity of solution) of the synthesized polymer [Fig.2 (1)]. As can be seen from Fig.3, the effect of the reaction time differs, depending on the temperature. At elevated temperatures (230, 270°C) the process is rapid, leading to the formation of products with sufficiently high viscosity of their solutions, which can be further enhanced by prolonging the heating time and /105 working in vacuum. Conducting the reaction at 290°C leads to the formation of insoluble products. At 200°C, the viscosity of solutions of the synthesized polymers is quite low and continues to decrease with increasing reaction time. On the basis of these findings, the process of formation of polybenzimidazoles may be represented as a two-stage reaction that follows Scheme I.



Scheme I

During the first stage, polyaminoamide forms and during the second the imidazole ring is closed under liberation of water. The results of an elementary analysis of polymers synthesized at various temperatures provide proof

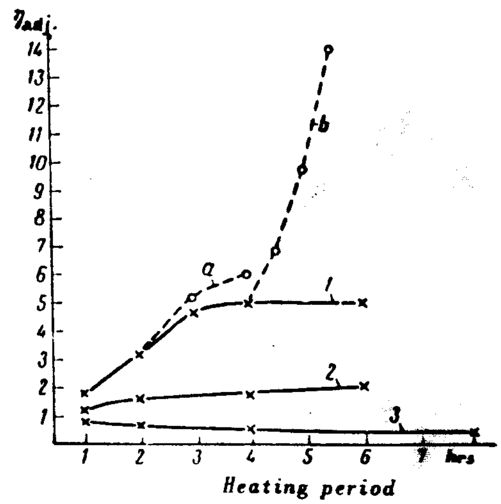
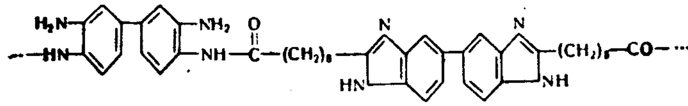


Fig.3 Adjusted Viscosity of Polymer Solution in Formic Acid as a Function of Reaction Time
1 - At 270° C; 2 - At 230° C; 3 - At 200° C; the solid lines represent polymers obtained at atmospheric pressure and the broken lines, polymers obtained in vacuo;
a - 10^{-2} mm Hg; b - 10^{-3} mm Hg.

for this mechanism. The elementary composition of the product obtained at 200° C corresponds to the polyamide link; at 270° C it approaches the configuration of the link of the corresponding polybenzimidazole. As for the polymers synthesized at intermediate temperatures, judging from the findings of elementary analysis, they contain links of both types; in this connection, as the reaction temperature is increased from 230° to 270° C, the content of imidazole rings in the synthesized polymers increases. Clearly, the closing of the imidazole rings is assisted by the higher temperature. At low temperatures, the reaction is mainly oriented toward the formation of polyamide chains.

Thus, the macromolecule of the reaction product contains both amide and /106 imidazole groups, whose mutual ratio changes in the course of the reaction



This would account for the decrease in viscosity of the polymer solutions during the reaction at 200° C; the formed polymers represent nearly homogeneous polyamides. The decrease in their viscosity with heating time is attributable to their destruction by the phenol, simultaneously released in the course of

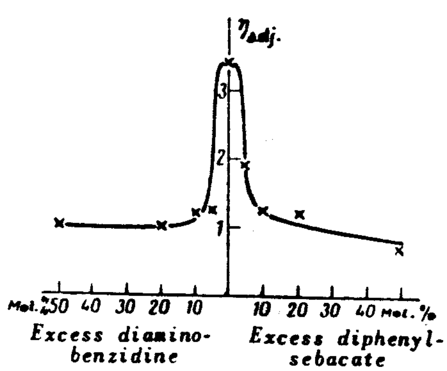


Fig.4 Effect of an Excess of Source Reagents on the Adjusted Viscosity of a Solution of Poly-2,2'-(Octamethylene)-5,5'-Dibenzimidazole in Formic Acid

the reaction, which at 200° C is very slowly eliminated from the reaction range. Imidazole rings are much more stable and are not destroyed under these conditions. The formation of insoluble products, when the reaction is conducted at 290° C, is obviously attributable to the linking of macromolecules which may occur under these conditions owing to several reactions of which the most probable are the reamidation reaction between NH_2-groups and amide groups and the interaction between NH_2-groups leading to the formation of secondary amino groups. The occurrence of reactions due to the NH-groups of the imidazole ring also is possible.

The investigated process obviously cannot be regarded as a conventional type of equilibrium polycondensation, i.e., polycondensation characterized by the presence of an equilibrium state which sets in as a result of direct processes of polycondensation and reverse processes of destruction of the resulting macromolecules.

The process of the formation of polybenzimidazoles is distinguished by its great complexity. During the first stages, when the formation of aminoamide links chiefly takes place, the reaction is clearly of the equilibrium kind and obeys the laws characteristic of equilibrium polycondensation. This pertains in particular to the effect of an excess of reagents (Fig.4) and to the addition of monofunctional compounds (Figs.2, 3, 4). This is accompanied by the cessation of chain growth, typical of equilibrium polycondensation (Bibl.3, 4). On the other hand, here and in the case of an excess of one of the source reagents, the processes of the acidolysis and aminolysis of the polymer chains are clearly possible, since, as pointed out above, they contain polyamide links to a greater or smaller degree.

During later stages of the reaction, when the macromolecules contain chiefly benzimidazole rings, the process distinctly loses to an increasing extent its equilibrium character, since benzimidazole rings are extremely stable and are not destroyed under the reaction conditions.

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